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## VERIFICATION OF A TRANSLATION

I hereby declare that I am knowledgeable in the French language in which the below identified application was filed, and that to the best of my knowledge and belief, the English translation of the International patent application n° PCT/FR 98/01872 is a true and complete translation of the above identified international patent application as filed.

Date : February 21, 2000

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For and on behalf of Cabinet LAURENT & CHARRAS

PAPER OR BOARD WITH IMPROVED PRINTABILITY

5           The invention relates to a paper or board with improved printability, intended to be printed by gravure or flexographic printing. It also relates to the process for manufacturing such a paper or board.

10           Gravure and flexographic printing are printing techniques well known to those skilled in the art.

15           Gravure printing essentially consists in pressing the paper to be printed onto an etched cylinder, the surface of which consists of a multitude of cells having a size of approximately 30 to 100 micrometres which are filled with fluid ink. Because of its fluidity, the surface of the ink forms a meniscus inside each cell, which meniscus tends to deform during rotation of the cylinder and thus reduce the contact between the ink and the paper to be printed.

20           Flexographic printing is a process which relies on the same principles as those of gravure printing, apart from the fact that the printing elements instead of being in the form of hollows are in relief. As previously, the quality of the printing depends on there being intimate contact between the ink and the paper.

30           Moreover, it is known that for certain "high-performance" papers, especially those whose coating composition includes a high proportion of binders together with specific additives, as well as for coated boards, it is often difficult to achieve good printability when printing by the gravure or flexographic process.

35           The problem posed is therefore that of improving the printability of papers printed by the gravure or flexographic printing technique while seeking to improve the contact between the ink and the paper.

To improve the printability, two different techniques are available:

- 5       - increasing the coat weight, whether in the case of a single-ply paper or in the case of a two-ply paper;
- 10       - improving the surface finish of the single-ply or two-ply paper by a mechanical calendering action, that is to say by making the coated sheet pass, with pressure applied, between heated metal rollers and resilient rollers, this corresponding to a supercalendering or "soft-calendering" operation.

3       The technique consisting in increasing the weight of the coat is not satisfactory in so far as it cannot be applied in order to obtain papers with a low grammage, for example about 40 to 45 g/m<sup>2</sup>, the mechanical properties of which would be too greatly affected by the increase in the weight of the coat to the detriment of the fibrous mass. Furthermore, 15 increasing the grammage of the paper or of its coat inevitably leads to a reduction in the folding resistance.

20       Moreover, and above all, even if the printability is improved it still remains, however, insufficient and the increase in coating weight in the first case or the calendering operation in the second case inevitably results in the porosity being reduced and therefore the paper being closed to the air, whereas as high as possible a porosity is absolutely 25 essential for certain high-performance papers, such as those complexed with barrier materials. The term "barrier materials" should be understood to mean materials which form in particular, a barrier to greases, to gases and to water and water vapour, such as polyethylene, polypropylene or polyester films or an 30 aluminium foil, for example paper-aluminium-polyethylene assemblies.

35       This is because these complexes, used in packaging, are generally subjected to heat-sealing

operations, for example polyethylene-polyethylene heat sealing in the abovementioned case, often causing the appearance of a blistering phenomenon. More specifically, the heat-sealing operation may cause blisters or air bubbles to form, these being due to the vaporization of the water contained in the paper, the solvent or the size. In the case of a paper of low porosity, the vapours formed cannot escape through the latter, therefore causing the paper medium to separate from the barrier coat in the welding zones.

In order to avoid the blistering phenomenon, it is necessary to use a single-ply paper, that is to say a medium coated with a pigment-based coat, which paper has good porosity, especially compared with a two-ply paper. Even though the porosity is satisfactory and the paper consequently exhibits good resistance to blistering in the possibly heat-sealed zones, its printability unfortunately remains inadequate.

One is therefore confronted with two main problems, namely that of improving the printability on the one hand and that of maintaining the level of porosity of a single-ply paper on the other hand, for which problems the solutions proposed hitherto have a radically opposite effect since use is made in the first case of an increase in the coating weight and in the second case of densification, these two solutions resulting in a reduction in the porosity.

In other words, none of the techniques described above - whether increasing the weight of the coat, the double coating or the calendering of a single-ply or two-ply paper - allows the printability of the paper to be improved without considerably reducing its porosity.

A paper intended to be printed by flexographic printing has also been proposed in document EP-A-0,337,771. That document describes, in its Example 1, a medium coated with two coats, respectively a first coat based on bentonite and a second coat consisting of an aqueous solution of kaolin and of an acrylic

copolymer. As the results show, the percentage of missing dots remains relatively high (about 5%) so that the printability cannot be regarded as being satisfactory.

5           Moreover, document FR-A-1,449,148 describes a printing paper covered with a double layer of a light coating in which the first coat consists of an aqueous stock containing 15 to 50% satin white. In addition, it is mentioned that the paper is necessarily calendered  
10 after coating with the first coat, thereby increasing the number of steps needed in the manufacturing process.

          At the same time, attempts are made in some applications to reduce the grammage of the product  
15 obtained without correspondingly degrading the mechanical properties, this being done, in particular, for economic reasons. Nevertheless, in some cases, attempts are made to reduce only the grammage of the coating so as to be able to transfer this weight saving  
20 to the fibrous medium, thus allowing the mechanical properties of the final product to be enhanced.

          The subject of the invention is therefore a novel type of paper intended to be printed by gravure or flexographic printing, making it possible to solve  
25 all the problems briefly mentioned above and especially:

- to improve the printability by seeking to increase the contact between the ink and the paper medium,
- 30   - to maintain the porosity, particularly in the case of complexed high-performance papers and
- optionally, to reduce the grammage of the product obtained without degrading its mechanical properties.

35           To solve the problem relating to printability, the invention proposes a paper or board with improved printability which is intended to be printed by gravure or flexographic printing and consists of a fibrous

medium coated with at least one conventional surface coat.

5 This paper or board is characterized in that it includes, between the fibrous medium and the conventional surface coat, a coat of a composition based on specific pigments and intended to improve the contact between the conventional surface coat and the printing ink, the said composition on the one hand including at least one pigment chosen from the group  
10 comprising silica, precipitated calcium carbonate (PCC) and calcined kaolin, on their own or as a mixture, and on the other hand being deposited on the fibrous medium in an amount not exceeding five grams per square metre (5 g/m<sup>2</sup>).

15 In the rest of the description and in the claims, the term "conventional surface coat" should be understood to mean a surface coat comprising pigments, binders and additives, having characteristics suitable for the subsequent application, for example paper for  
20 packaging, printing paper for publishing, paper for complexing, board, etc. The compositions of these conventional surface coats therefore depend on the application envisaged and are perfectly well known to those skilled in the art.

25 In other words, the invention consists in inserting, between the fibrous medium and the conventional surface coat, whether in the case of a single-ply or two-ply paper or board, a very small quantity of a composition comprising pigments having  
30 specific properties, which, by allowing the surface of the conventional coat to be improved, makes it possible for the printability to be improved spectacularly, by virtue of a more regular contact with the printing ink. At the same time, depositing the composition of the  
35 invention on the fibrous medium makes it possible for the said medium to have a very uniform surface microporosity, which also helps to improve the printability.

Furthermore, the improvement in printability is so great, even when the composition of the invention is deposited on the fibrous medium in a very small amount, that it is possible to reduce the amount of the conventional coat deposited, thereby resulting not only in a marked reduction in the grammage of the final paper (by approximately 10%), without thereby degrading its mechanical properties, but also, depending on the choice of pigment, in the porosity of the paper or board obtained being maintained or even improved. The reduction in the amount of conventional coat deposited also makes it possible, in some cases, to correspondingly increase the mass of the fibrous medium, giving the final paper superior mechanical properties, especially in terms of stiffness, tensile strength, burst strength and tear strength.

At the same time, the fact of decreasing the coat weight makes it possible to reduce the phenomenon of breaking at folds, which becomes more prevalent the higher the coat weight.

Furthermore, the nature of the composition of the invention is independent of that of the conventional coat applied, so that it can be used whatever the intended subsequent application.

In the process of the invention, it is possible to use any type of silica chosen from the group comprising colloidal, precipitated or pyrogenic silicas.

It has been found that very good results are obtained using precipitated silicas having a specific surface area of between 150 and 250 m<sup>2</sup>/g.

Likewise, among the precipitated calcium carbonates, a colloidal calcium carbonate advantageously having a specific surface area of between 25 and 40 m<sup>2</sup>/g may be used.

Finally, the term "calcined kaolin" should be understood to mean a kaolin calcined at a temperature of about 1000°C, resulting in a disintegration of the

aggregates forming the kaolin and in the removal of water from the aluminium silicate.

When the said composition based on specific pigments is deposited in an amount greater than 5 g/m<sup>2</sup>,  
5 the beneficial effect on the printability remains but the product becomes less beneficial, not only economically but also due to the fact that the weight of the finished paper increases.

According to one advantageous embodiment, the  
10 composition based on specific pigments is deposited on the fibrous medium in an amount of at least one gram per square metre, advantageously between 1 and 3 g/m<sup>2</sup>.

For an amount deposited of less than 1 g/m<sup>2</sup>, it is found in fact that the printability characteristic  
15 is not improved significantly.

In order both to improve the printability and to maintain or improve the porosity compared with a single-ply paper, the composition based on specific pigments consists exclusively of silica.

This is because it has been found that, very  
20 surprisingly, this pigment allows the two objectives to be achieved at the same time, this being so even for a very small amount deposited on the fibrous medium. It follows that the paper obtained is suitable in  
25 particular for the manufacture of high-performance paper subjected to heat-sealing operations before complexing and therefore liable to be subject to blistering phenomena.

The invention also relates to a process for the  
30 manufacture of a paper or of a board, intended to be printed by gravure or flexographic printing, which consists:

- in producing a fibrous medium from a paper suspension,
- 35 • then in coating the medium with at least one conventional surface coat,
- in drying the paper or the board thus formed,
- and finally in calendering the paper or board obtained.



This process is characterized in that:

- at least five grams per square metre ( $5 \text{ g/m}^2$ ) of a composition based on specific pigments chosen from the group comprising silica, precipitated calcium carbonate and calcined kaolin, on their own or as a mixture, are deposited beforehand on the fibrous medium;
- and then the fibrous medium thus covered is dried before it is coated with the conventional surface coat.

As already stated, the composition is deposited on the fibrous medium in an amount not exceeding  $5 \text{ g/m}^2$ , thereby also making it possible to reduce the grammage of the traditional coat and thus increase the mass of the fibrous base medium and therefore the mechanical properties of the final paper or board.

Advantageously, the composition based on specific pigments is deposited on the fibrous medium by coating, all of the operations being carried out under the usual conditions for manufacturing a coated paper or board.

Furthermore, the deposition of the composition based on specific pigments on the fibrous medium followed by the coating with the conventional coat are carried out using a conventional coater or a size press, or a metering size press (MSP). The two coating operations are carried out either on or off a paper machine.

With regard to the calendering step, this is carried out by means of a soft calender or a supercalender under the conventional conditions of manufacturing coated paper.

As already stated, a very marked improvement is found in the quality of the surface of the conventional coat on media precoated with the composition based on specific pigments of the invention.

In particular, the process described above allows a paper of low grammage to be manufactured which

has excellent printing properties in gravure or flexographic printing.

Nevertheless, it is also possible to manufacture, using the same process, a paper of high grammage having good porosity as well as good printability, whatever the printing process.

The way in which the invention is realized and the advantages which stem therefrom will become more clearly apparent from the various illustrative examples which follow.

Comparative Example 1

The printability and porosity values of a single-ply paper, of a two-ply paper and of a paper characteristic of the invention are compared, the common point of which is to present a conventional surface coat of the same composition.

• **Composition and preparation of the single-ply paper**

A coating slip is prepared, the composition of which, given in dry/dry parts by weight, is shown in the table below:

Pigments	AMAZON 90 (kaolin) <sup>1</sup>	85
	SATIN WHITE <sup>2</sup>	15
Binder	ACRONAL A 360 D <sup>3</sup>	14
Thickener	RHEOCOAT 35 <sup>4</sup>	0.4
Insolubilizing agent	URECOLL SU <sup>5</sup>	2.3
Dispersant	GX <sup>6</sup>	0.2
Lubricant	CECAVON CA 350 <sup>7</sup>	1

1: registered trade mark, product sold by Kaolin d'Arvor

25 2: product sold by Suprasmit

3, 5: registered trade marks, products sold by BASF

4, 6: registered trade mark, products sold by Coatex

7: registered trade mark, product sold by Elf Atochem

By coating by means of a coater of the metal-blade type, 12.1 g/m<sup>2</sup> of the composition thus

prepared are deposited on a fibrous medium manufactured beforehand. The paper obtained is dried and calendered.

• Composition and preparation of the two-ply paper

A first coating slip, corresponding to the first ply, is prepared, the composition of which, given in dry/dry parts by weight, is shown in the table below:

Pigment	OMYALITE 90 (natural calcium carbonate) <sup>8</sup>	100
Binder	ACRONAL A 360 D	13
Thickener	RHEOCOAT 35	0.4
Insolubilizing agent	URECOLL SU	0.8
Dispersant	GX	0.1

8: registered trade mark, product sold by OMYA

Using a coater with a metering bar or metal blade, 6.3 g/m<sup>2</sup> of the coating slip thus prepared are deposited, on a paper machine, onto a fibrous medium manufactured beforehand.

After this coat has been dried, a second coating slip is coated in line, the composition of which corresponds to that used in the above single-ply paper.

Using a coater with a metal blade, 8.1 g/m<sup>2</sup> of this coating slip are deposited on the first coat.

The paper obtained is dried and calendered under the same conditions as previously.

• Composition and preparation of the paper of the invention

5 The composition corresponding to the paper of the invention is prepared, the characteristics of which are shown in the table below:

Pigment	SK 300 DS <sup>9</sup> (precipitated silica)	100
Binder	ACRONAL A 360 D	60
Insolubilizing agent	URECOLL SU	1
Dispersant	GX	0.1

9: registered trade mark, product sold by Degussa

10 The specific surface area of the silica used is approximately 200 m<sup>2</sup>/g.

Using a coater with a metering bar, 2.9 g/m<sup>2</sup> of the composition thus prepared is deposited on a fibrous medium.

15 After drying, 8 g/m<sup>2</sup> of a coating slip, the composition of which is identical to that of the single-ply paper manufactured previously, are deposited.

20 Next, the paper obtained is dried and calendered under the same conditions as previously.

The printability and porosity results of the various papers thus manufactured are given in the table below.

25 The printability is evaluated using the Heliotest technique, which consists in measuring the distance of the twentieth missing dot on the printing of a paper strip using an apparatus known by the name "IGT Analyser". The results are given in millimetres.

30 The SCAN porosity is measured using the Lorentzen technique. The results are given in cm<sup>3</sup>/m<sup>2</sup>.s.

	Single-ply paper	Two-ply paper	Paper of the invention
Heliotest printability (mm)	23	18	82
Porosity	820	630	1100
Blistering resistance at 190°C after complexing with 18 $\mu$ m aluminium	blistering	blistering	no blistering
Grammage of the coated paper (g/m <sup>2</sup> )	67	69.3	65.8
Total coat weight (g/m <sup>2</sup> )	12.1	14.4	10.9

A great improvement in printability may therefore be seen in the case of the paper of the invention. In addition, the printability is improved despite an extremely small amount of the composition being deposited, about 3 g/m<sup>2</sup>. This small amount of composition deposited makes it possible to significantly reduce the weight of the conventional coat (10.9 g/m<sup>2</sup>) and therefore to markedly improve the porosity (1100) compared with that of a conventional single-ply paper (820). It follows that no blistering is observed with the paper of the invention when this is a complexed paper subjected to a heat-sealing operation.

It should be noted that the standard two-ply paper has the level of printability of the single-ply paper despite a greater total coat weight. This result is not surprising in so far as the standard double coating does not always increase the printability for low coat weights, of less than 16 g/m<sup>2</sup>, because of the

need to dilute the coating baths in order to limit the amount of coating deposited.

Comparative Example 2

5

The printability and porosity values of three two-ply papers and three papers characteristic of the invention are compared, the conventional surface coat of which has three different compositions.

10

Shown in the following table is the composition, given in dry/dry parts by weight, of these three conventional surface coats:

		Surface coat 1	Surface coat 2	Surface coat 3
Pigment	AMAZON 90	88	50	100
	OMYALITE 90	12	50	---
Binder	ACRONAL A 360 D	13	13	13
Thickener	RHEOCOAT 35	0.4	0.4	0.4
Lubricant	CECAVON CA 350	1	1	1
Insolubilizing agent	URECOLL SU	0.7	0.7	0.7
Dispersant	GX	0.1	0.1	0.1

15

• **Composition and preparation of the two-ply paper**

A coating slip is prepared, the composition of which, given in dry/dry parts by weight, is shown in the following table:

20

25

Pigments	AMAZON 90	34
	OMYALITE 90	66
Binders	ACRONAL A 360 D	13
	ACTISIZE 80 <sup>10</sup>	11
Lubricant	CECAVON CA 350	0.3
Insolubilizing agent	URECOLL SU	1
Dispersant	GX	0.1

10: registered trade mark, product sold by Roquette

A fibrous medium prepared beforehand is coated with the coating slip thus prepared, in an amount of 9 g/m<sup>2</sup>, using a coater with a metering bar or a metal blade.

Next, 10 g/m<sup>2</sup> of the surface coat 1 are deposited using a coater of the metal-blade type.

Next, two other two-ply papers are manufactured with the surface coat 2 and then with the surface coat 3, both coats being deposited in an amount of 10 g/m<sup>2</sup> on the first coat.

#### • Composition and preparation of the paper of the invention

A coating slip is prepared, the composition of which, given in dry/dry parts by weight, is:

Pigment	SK 300 DS	100
Binder	ACRONAL A 360 D	20
	ACTISIZE 80	20
Lubricant	CECAVON CA 350	0.3
Insolubilizing agent	URECOLL SU	1
Dispersant	GX	0.1

Using a coater of the metering-bar type, 3 g/m<sup>2</sup> of this coating slip are deposited on a fibrous medium manufactured beforehand.

After drying, the surface coat 1 is deposited.

The same operation is repeated with the surface coats 2 and 3, all three coats being deposited in an amount of 10 g/m<sup>2</sup> on the first coat, using a coater with a metal blade.

After drying and calendering under identical conditions, the Heliotest printability results and the SCAN porosity of the various papers obtained were evaluated.

10

	Two-ply paper			Paper of the invention		
	Surface coat 1	Surface coat 2	Surface coat 3	Surface coat 1	Surface coat 2	Surface coat 3
Heliotest printability	25	37	38	> 110	> 110	> 110
SCAN porosity	160	150	200	1100	930	1500
Total coat weight (g/m <sup>2</sup> )	19	19	19	13	13	13
Grammage of the final paper (g/m <sup>2</sup> )	95	95	95	89	89	89

It may thus be seen that the paper of the invention exhibits excellent printability compared with a conventional two-ply paper, this being so with a surface coat of identical composition. In addition, the coat weight is markedly less than that of a two-ply paper so that the grammage of the final paper is correspondingly reduced. Likewise, it will be noted that the paper of the invention has an excellent porosity. Excellent Heliotest results (>110) are also obtained with the paper of the invention, whatever the



pigmentary composition of the surface coat. The invention therefore makes it possible to modify, in a very flexible manner, the nature of the composition of the surface coat, and in particular makes it possible to choose inexpensive, or whiter, pigments, or else those which are favourable to the development of a glossy or matt surface, while still ensuring good printability.

10      Comparative Example 3

15      The printability and porosity values of a single-ply paper and of a paper characteristic of the invention are compared, the composition of which paper characteristic of the invention, covering the fibrous medium, contains pigments of different type.

• Composition and preparation of the single-ply paper

20      A fibrous medium prepared beforehand is coated with a conventional coat, the composition of which is:

Pigments	AMAZON 90 (kaolin) <sup>1</sup>	85
	SATIN WHITE <sup>2</sup>	15
Binder	ACRONAL A 360 D <sup>3</sup>	16
Thickener	RHEOCOAT 35 <sup>4</sup>	0.3
Lubricant	CECAVON CA 350 <sup>7</sup>	0.9

25      Using a coater with a metering bar, 8.9 g/m<sup>2</sup> of this coating slip are deposited on the fibrous medium. Next, the medium is dried and calendered.

• Composition and preparation of the paper of the invention

5 Three different compositions, identified below by the references A, B, C, are prepared.

Composition A

Pigment	SK 300 DS	100
Binder	ACRONAL A 360 D	60
Insolubilizing agent	URECOLL SU	1

10

Using a coater with a metering bar, 2.2 g/m<sup>2</sup> of this composition are deposited on the fibrous medium.

After drying, the conventional coat, the composition of which is identical to that of the  
15 single-ply paper prepared beforehand, is then coated in an amount of 7.8 g/m<sup>2</sup>.

Composition B

Pigment	COLLOIDAL PCC <sup>11</sup> (precipitated calcium carbonate)	100
Binder	ACRONAL A 360 D	20
Insolubilizing agent	URECOLL SU	1

20

11: registered trade mark, product sold by Faxo Kalk

Using a coater with a metering bar, 2.3 g/m<sup>2</sup> of this composition are deposited on the fibrous medium.

After drying, the conventional coat prepared  
25 for the single-ply paper is coated in amount of 7.8 g/m<sup>2</sup>.

*Composition C*

Pigment	COLLOIDAL PCC	50
	SK 300 DS	50
Binder	ACRONAL A 360 D	20
Insolubilizing agent	URECOLL SU	1

Using a coater with a metering bar, 2.6 g/m<sup>2</sup> of this composition are deposited on the fibrous medium.

After drying, the conventional coat, the composition of which is identical to that of the single-ply paper prepared beforehand, is coated in amount of 6.2 g/m<sup>2</sup>.

The printability and porosity results of the various papers obtained are given in the following tables.

	Single-ply paper	Paper A	Paper B	Paper C
Printability (Heliotest)	18	94	49	63
Porosity	760	570	480	290
Total coat weight (g/m <sup>2</sup> )	8.9	10	10.2	8.8
Paper grammage (g/m <sup>2</sup> )	46	46.5	46.5	70

It may therefore be seen that the printability of the paper of the invention is improved significantly over a single-ply paper.

Depending on the choice of the pigments of the composition of the invention, it is possible either to favour increase in printability (papers A, C) or to favour the high retention of porosity (paper A). Paper

A makes it possible to achieve both these objectives and can be used in particular for the manufacture of high-performance papers. In cases where the porosity is not of concern, the other pigments may be chosen.

5           It is therefore apparent from the description that the invention has many advantages.

          This is because it provides a paper for gravure or flexographic printing which has greatly improved printability compared with the single-ply and two-ply  
10 papers known hitherto, while still preserving a porosity close to that of a single-ply paper.

          Consequently, this invention can be used in many applications, especially when it is necessary to add a barrier material, such as aluminium,  
15 polyethylene, polypropylene or polyester, to a coated paper without the risk of the blistering phenomenon occurring during heat sealing.

          Likewise, the low grammage of the composition incorporated between the fibrous medium and the  
20 standard conventional coat not only allows the grammage of the final paper to be appreciably decreased but also, in some cases, allows the weight of the fibrous medium to be increased, so as to improve its mechanical properties.

25           Likewise, the reduced grammage of the finished paper makes it possible to avoid the phenomena of breaking at folds.

          Moreover, this paper can be manufactured by a process involving standard techniques, such as coating  
30 using a coater, a size press or a metering size press (MSP).

          Thus, complexes are obtained which may be used in food packaging, the printability and heat-sealing properties of which are greatly improved.